Sampling of Aryldiazonium, Anilino, and Aryl Radicals by Membrane Introduction Mass Spectrometry: Thermolysis of Aromatic Diazoamino Compounds

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Membrane introduction mass spectrometry (MIMS) is used to sample free radicals generated by thermolysis at atmospheric pressure. This is done by heating the solid sample in a custom-made probe that is fitted with a silicone membrane to allow selective and rapid introduction of the pyrolysates into the ion source of a triple quadrupole mass spectrometer. Phenyldiazonium radical ($C_6H_5N_2$) and some of its ring-substituted analogs, the methoxy anilino radical $CH_3OC_6H_4NH$, and aryl radicals are generated by gas phase thermolysis of symmetrical aryl diazoamino compounds (ArNH–N$_2$Ar). The radicals are identified by measurement of their ionization energies (IE) using threshold ionization efficiency data. A linear correlation between the ionization energy of the phenyldiazonium radicals and their Brown σ^+ values is observed, and this confirms the formation of these species and validates the applicability of MIMS in sampling these radicals. The ionization energies of the aryldiazonium radicals are estimated as IE (p-CH$_3$O–C$_6$H$_4$N$_2$), 6.74 ± 0.2 eV; IE (p-CH$_3$–C$_6$H$_4$N$_2$), 7.72 ± 0.2 eV; IE (C$_6$H$_5$N$_2$), 7.89 ± 0.2 eV; IE (m-Cl–C$_6$H$_4$N$_2$), 7.91 ± 0.2 eV; IE (p-F–C$_6$H$_4$N$_2$), 8.03 ± 0.2 eV; and IE (m-NO$_2$–C$_6$H$_4$N$_2$), 8.90 ± 0.2 eV. The ionization energies of the aryl radicals are estimated as IE (p-CH$_3$O–C$_6$H$_4$), 7.33 ± 0.2 eV; IE (p-CH$_3$–C$_6$H$_4$), 8.31 ± 0.2 eV; IE (C$_6$H$_5$), 8.44 ± 0.2 eV; IE (m-Cl–C$_6$H$_4$), 8.50 ± 0.2 eV and IE (p-F–C$_6$H$_4$), 8.54 ± 0.2 eV. Also, the ionization energy of the p-methoxyanilino radical (p-CH$_3$O–C$_6$H$_4$NH) is estimated as 7.63 ± 0.2 eV. (J Am Soc Mass Spectrom 1998, 9, 234–241) © 1998 American Society for Mass Spectrometry
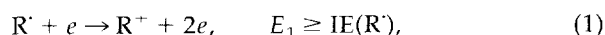
The importance of free radicals in biological processes [1a], catalysis [1b], and carcinogenesis [1c], and as reactive intermediates in gas phase [2a], solution [2b], and solid-state reactions [2c], is well established [3]. Since the definition of the radical by Lavoisier in 1793 [4], and the discovery of the first free radical, triphenylmethyl, by Gomberg in 1900 [5], many stable free radicals have been generated in solution and in the gas phase and their physical and chemical properties have been investigated. Mass spectrometry has proven to be a useful tool in the detection of free radicals [6–8], in the determination of the rates of their reactions [9] and in elucidation of their structures [10]. Free radicals are also common products of fragmentation processes in the mass spectrometer. The use of membrane introduction mass spectrometry (MIMS) to directly determine free radical species present in a

gaseous reaction medium and to study their ionization energies is the particular objective of this investigation.

Pioneering work in the development of mass spectrometry as a sampling tool for the study of free radical intermediates in chemical reactions was performed by Eltenton [11]. Since then, mass spectrometry has been used effectively for the detection of free radicals in heterogeneous and homogeneous thermal reactions [11, 12], in electric discharges [13], in flames [14], and in bimolecular [15] and photolytic reactions [16]. When sampling free radicals using mass spectrometry, it is essential to differentiate the ionic signals that arise from ionization of free radicals from those due to the same ions that result from fragmentation processes. In particular, when radicals (R) are generated by thermal decomposition, some of the parent compound (RX) can also enter the ion source of the mass spectrometer without undergoing pyrolysis. Thus, the compounds that are introduced into the electron ionization (EI) source of the mass spectrometer include the neutral molecule RX and the radical (R). Consequently, the

ionic species R^+ may be formed by the following two electron impact processes: (i) homolysis of RX to generate the radical $(R^.)$ which is then ionized (eq 1) or (ii) ionization of RX to give $(RX^{+.})$ which then undergoes cleavage to give R^+ (eq 2):

$$R^. + e \rightarrow R^+ + 2e, \qquad E_1 \geq IE(R^.), \qquad (1)$$

$$RX + e \rightarrow R^+ + X^. + 2e, \qquad E_2 \geq IE(R^.) + D(R\text{-}X) \quad (2)$$

In these equations, E_1 and E_2 denote the minimum energies required to generate the ionized radical in reactions 1 and 2, $IE(R^.)$ denotes the ionization energy of the radical and $D(R\text{-}X)$ denotes the dissociation energy of the parent compound, respectively. Note that in favorable cases, the question of whether the ionic species R^+ is formed from process 1 or 2 can be resolved by measuring the appropriate minimum energy values using ionization efficiency curves. If the radical has a measured threshold energy lower than the IE of RX, then $R^.$ must be generated (at low electron energies at least) by ionization of the radical [17].

The design of sampling systems for the detection of free radicals is a challenging task because of the reactive nature, limited lifetimes, and low concentrations of radicals in the reaction medium. In spite of continued improvements in experimental design [11–16], a system that can rapidly analyze free radicals, withstand high pressure gradients, be easily operated, and provide the capability of sampling radical intermediates soon after their formation does not yet exist. In this study, the capability of membrane introduction mass spectrometry (MIMS) [18], a method that combines the versatility of mass spectrometry with the rapid sample introduction capability of membranes, is investigated to address the above issues.

Membrane introduction mass spectrometry is a relatively simple method that is flexible in terms of choice of membranes (amorphous silicone or microporous teflon, among many others; sheet or capillary configurations), is easily automated, and typically has a response for simple volatile organic compounds in water or air which is linear with concentration over a few orders of magnitude. The response time is typically less than a minute and detection limits are often in the ppb concentration range. MIMS has been adapted to various sample introduction systems, including flow injection analysis (FIA) procedures, and to different mass analyzers, including quadrupole, ion trap, and sector instruments. MIMS has been applied in environmental [19–21] and bioreactor [21] monitoring and the technique has been reviewed [19, 22–25]. Recently, Lewis and coworkers [26] used MIMS to study the stable nitrogen oxide radical $(NO^.)$ in solution and followed its kinetics in real time, but MIMS has not previously been used to study gas phase organic radicals.

Phenyldiazonium radicals $(C_6H_5N_2)$ are generated as reactive intermediates by pyrolysis of diazoamino compounds $(ArNH\text{-}N_2Ar)$ in a nitrogen atmosphere [27]. Although the mechanism of decomposition of aliphatic and aromatic diazoaminobenzenes in solution has been explored [28–30], no literature exists on the corresponding gas-phase mechanism. In this work, we use MIMS to sample for aryldiazonium and related radicals in the gas phase and confirm their presence using threshold energy measurements.

Experimental

A special direct insertion probe was built to generate free radicals by thermolysis. The probe is based on previously described membrane probes [see Figure 4, ref 18]. These were modified for this study to accept solid rather than fluid samples by removing the circulation ports for the analyte solution and providing an accessible chamber into which the solid could be loaded. A copper perforated ring was used as the probe tip instead of the perforated stainless steel tip previously described. The base of this chamber was made of copper to facilitate rapid heating using a cartridge heater; temperature was measured using a Pt resistance thermometer. The volume of the sample chamber was approximately 1 mL and the side facing the mass spectrometer ion source was sealed with a silicone membrane. The silastic membrane used was a 125 μ thick polydimethylsiloxane polymer (Dow Corning, Midland, MI). The analyte (20 μg) was loaded as the solid and pyrolyzed at atmospheric pressure by heating from ambient to 130°C in 6 s. In a few experiments, as noted, the probe was used as a direct insertion probe, without the membrane.

A Finnigan (San Jose, CA) TSQ 4500 triple quadrupole mass spectrometer was used for data acquisition. The operating conditions were 1850 V multiplier voltage, 100°C manifold temperature, 170°C source temperature, background pressure of 2×10^{-7} torr, scan rate 2 s/scan. Data were acquired by scanning the mass spectrometer over the mass-to-charge ratio range of 40–350. The electron energy was calibrated against a standard voltage source and corrected for a measured error of 0.2 eV.

For the threshold energy measurements, a reference compound, biphenyl was admixed with the analyte, and introduced into the ion source of the mass spectrometer via the pyrolysis membrane probe. The sample was rapidly heated to the desired temperature, near the decomposition temperature of the sample (e.g., 130°C for diazoaminobenzene), which was recognized by a sudden rise in the source pressure. The source pressure was maintained below 9×10^{-7} torr (nominal) to minimize errors that might occur due to ion/molecule reactions. It was observed that the sample rapidly desorbed within a few seconds, as monitored by the pressure increase and changes in mass spectra recorded continuously. A complete set of experiments was performed within 30 min and repeated on different days under identical conditions. Signal intensity versus ion-

Table 1. Synthesis and properties of symmetrical diazoaminobenzenes ArN = N–NHAr [32]

| Substituent | Melting point (°C) | | Reference |
	Experimental	Literature	
p-Methoxy	99.5–100	99.0–99.9	33
p-Methyl	115.5–116.5	117.3–117.9	33
None	98–98.5	99.3–100.3	33
m-Chloro	110–110.5	107	34
p-Fluoro	113–114	110	35
m-Nitro	194–195	194	36

izing electron energy measurements show data points that are the average of triplicate measurements performed on the same day. These measurements were made by varying the ionizing electron energy and plotting the current for the ion of interest as a fraction of that at 50 eV in a log-linear fashion. The linear portions of these curves (in the vicinity of 10^{-3}) were used to measure threshold energies relative to the ionization energy of the co-introduced reference compound, biphenyl, which has a known ionization energy of 8.16 ± 0.13 eV [31]. These procedures yielded appearance and ionization energies with a precision of ±0.07 eV, although the absolute uncertainty of the measurements is 0.2 eV, largely because of the uncertainty in the reference IE value. In cases in which the threshold energy plots gave nonparallel lines the values at 10^{-3} have been used.

Diazoaminobenzene and the corresponding aryl diazoamino compounds were synthesized using standard procedures [32–36]. A list of the compounds synthesized and their melting points is given in Table 1.

Results and Discussion

In order to pyrolyze diazoamino compounds at atmospheric pressure and efficiently sample the pyrolysate, a direct insertion pyrolysis/membrane probe was built. The silicone membrane chosen serves to selectively transfer small organic compounds, especially nonpolar compounds, into the ion source of the mass spectrometer. As such it is expected to discriminate against the air matrix present during the pyrolysis and to a smaller extent, against the reactant. The primary role of the membrane, however, is simply to provide a pressure differential and allow the products of atmospheric pressure pyrolysis to be sampled efficiently by the mass spectrometer. As in other applications, MIMS provides a convenient method of reproducibly introducing samples into the mass spectrometer.

Thermolysis of diazoaminobenzene and sampling of the pyrolysis products by MIMS yields a mass spectrum which includes m/z 105, corresponding to the phenyldiazonium cation ($C_6H_5N_2^+$), and m/z 77, the phenyl cation $C_6H_5^+$. As shown for the general case, in eqs 1 and 2, these ions might arise as products of dissociation of the intact diazoaminobenzene radical cation, or they

might be the products of ionization of the radicals, $C_6H_5N_2^-$ and $C_6H_5^-$, respectively. In order to determine whether the aryldiazonium and aryl radicals contribute to these signals, threshold energy measurements were made using biphenyl as calibrant. The results are shown in the form of a log-linear plot in Figure 1. The threshold energy values of the diazoaminobenzene radical cation (9.27 eV), the phenyldiazonium cation (7.89 eV), and the phenyl cation (8.44 eV) were measured by calibration against the known value of the IE of biphenyl [31]. The observed phenyldiazonium ion may arise by either of the two pathways shown (Scheme Ia and b). However, the fact that the phenyldiazonium cation has a threshold energy which is 1.38 eV lower than the IE of the parent diazoaminobenzene (9.27 eV), means that, at least at low electron energy, the phenyldiazonium cation cannot be formed by fragmentation of ionized diazoaminobenzene (Scheme Ia). The difference (1.38 eV) between the IE of diazoaminobenzene (9.27 eV) and the observed threshold energy of the phenyldiazonium cation is much too large to be an experimental uncertainty of the methodology (maximum estimated error is 0.4 eV). Hence, the phenyldiazonium cation observed at low electron energy must arise by Scheme Ib, i.e., by ionization of phenyldiazonium radical, and the measured energy value (7.89 ± 0.07 eV) corresponds to the IE of the phenyldiazonium radical.

Although threshold measurements are useful in differentiating the processes shown in Scheme Ia from Ib, there is a further complication that must be considered. The aryldiazonium radicals could also be generated by thermal decomposition of the neutral parent compound at the electron filament in the ion source of the mass spectrometer, i.e., the species that passes through the membrane might be the intact stable molecule and not the free radical. To test this and the ancillary possibility that thermal decomposition at the filament might be the source of the radicals of interest, the pyrolysis/membrane data for diazoaminobenzene were compared with those obtained using membrane sampling in the absence of thermolysis. This was achieved by slowly heating a sample of diazoaminobenzene to ensure continuous introduction of the parent in the vapor phase into the ion source of the mass spectrometer. Except for the change in the rate and the temperature of heating the experimental conditions were the same as those used in the standard pyrolysis/membrane experiments. No ions were observed at electron energies below the IE of the parent diazoaminobenzene compound (9.27 eV). This leads to the conclusion that the phenyldiazonium radicals are not being generated by thermolysis at the electron filament.

It might also be asked whether it is possible to perform the thermolysis experiment and sample the resulting radicals using a direct insertion probe, without using a membrane. This experiment was attempted but gave results which showed poor reproducibility. The characteristic rise and fall of source pressure indicated that thermolysis did occur and the mass spectra,
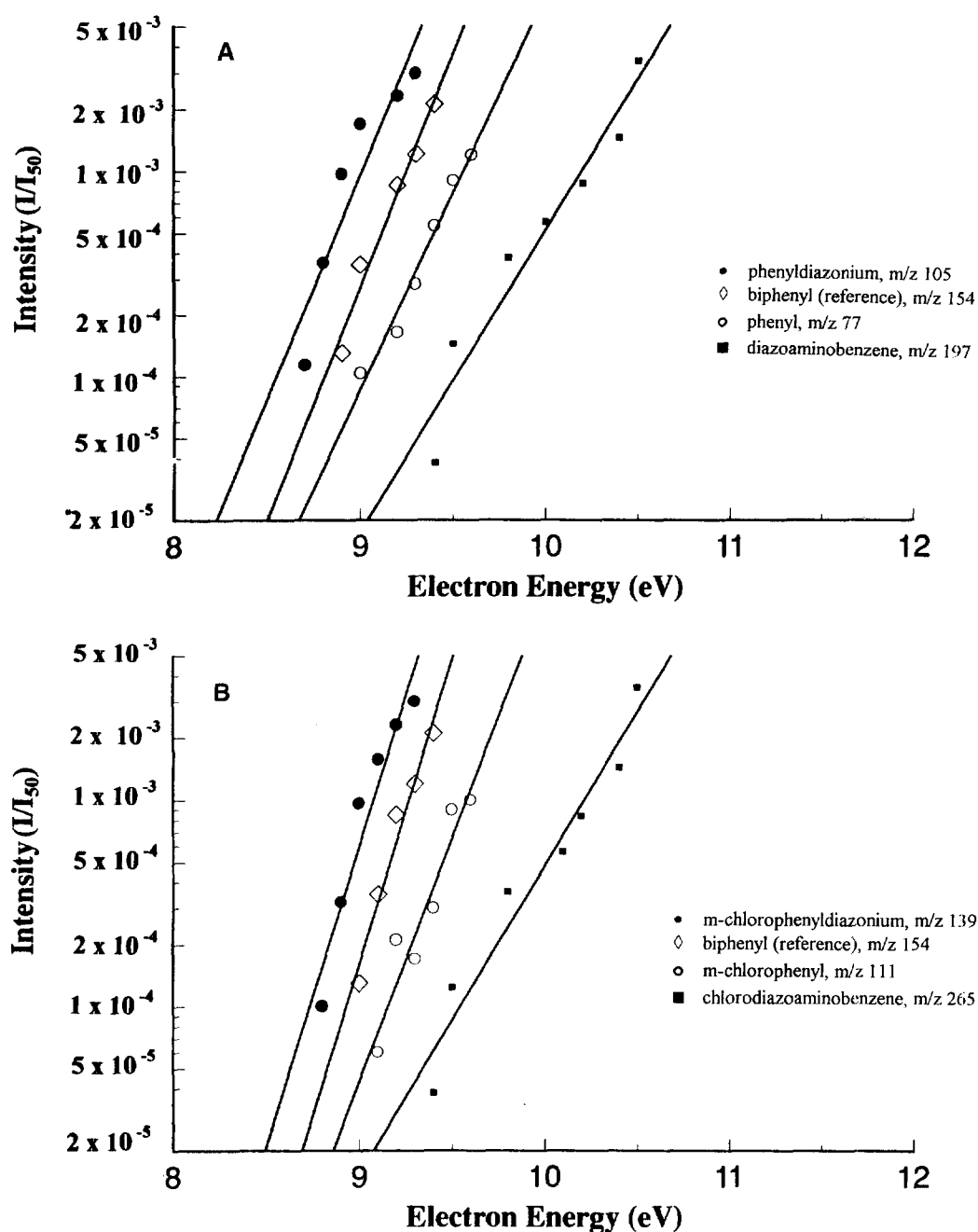
Figure 1. The ratio (I/I_{50}) of signal intensities (I) near threshold electron energy to that (I_{50}) at 50 eV plotted against electron energy for (a) phenyldiazonium cation (filled circle, m/z 105, IE = 7.89 eV), biphenyl radical cation (diamond, m/z 154, IE = 8.16 eV), phenyl cation (open circle, m/z 77, AE = 8.44 eV), and diazoaminobenzene radical cation (filled square, m/z 197, IE = 9.27 eV) on a log-linear scale. (b) m-Chlorophenyldiazonium cation (filled circle, m/z 139, IE = 7.91 eV), biphenyl radical cation (diamond, m/z 154, IE = 8.16 eV), m-chlorophenyl cation (open circle, m/z 111, AE = 8.50 eV), and bis(m-dichlorophenyl)diazoamino radical cation (filled box, m/z 265, IE = 9.46 eV) on a log-linear scale. The biphenyl radical cation (IE = 8.16 eV) was used as the calibrant in both experiments.

including those obtained at very low electron energy, indicate that the phenyldiazonium radical was generated. Note that the results of this experiment, considered in conjunction with those already presented, indicate that the lifetime of the aryldiazonium radical is at least a few seconds, as the typical membrane response

time for gas phase sampling of volatile compounds is on this order [19].

The methodology and results which demonstrate that the diazophenyl radical can be sampled using MIMS, applies with equal force to the substituted phenyldiazonium radicals for which threshold energy

(a)
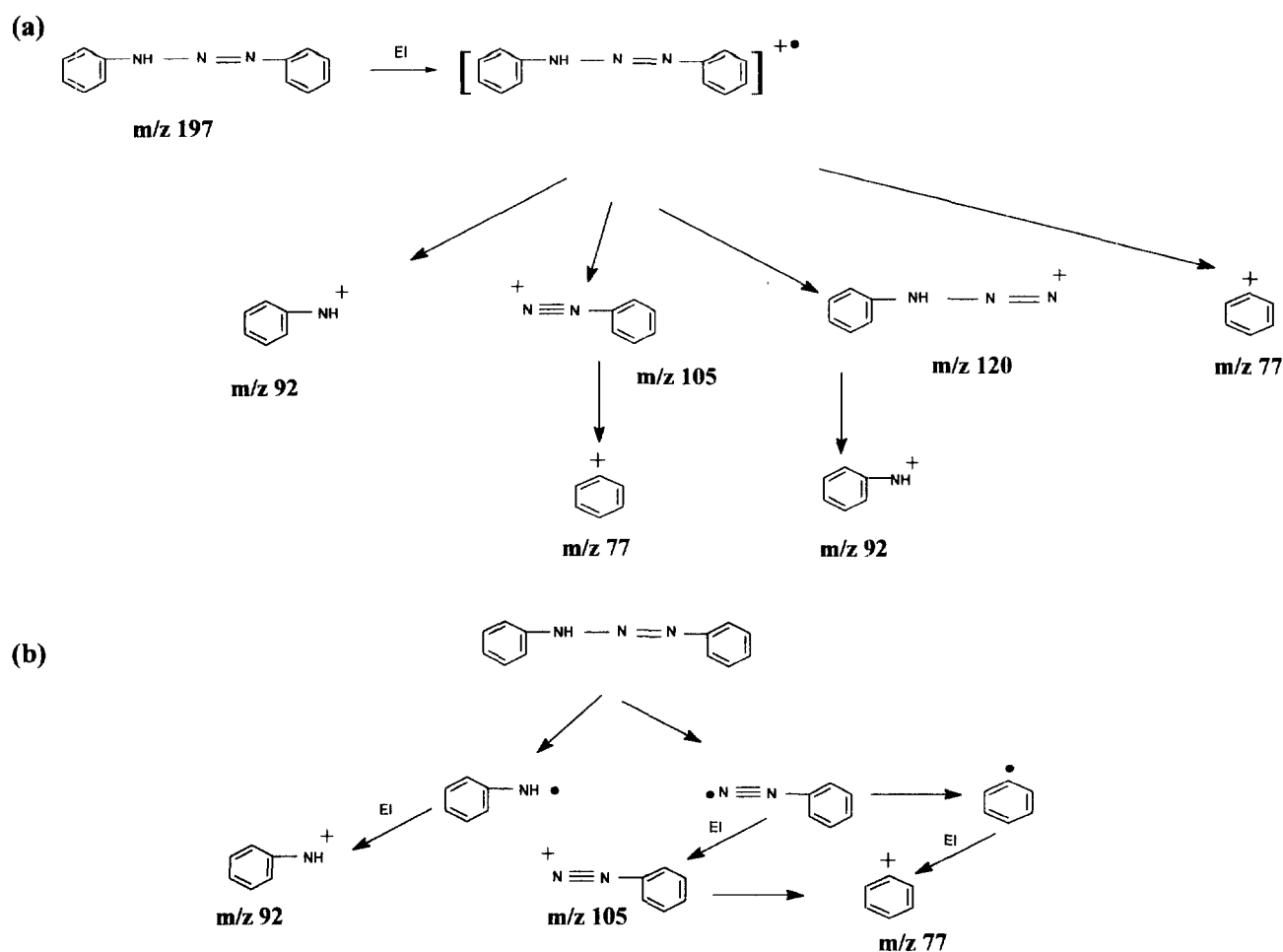
Scheme 1 (a). Fragmentation pathway for diazoaminobenzene

(b). Fragmentation pathways of the ionized pyrolysates of diazoaminobenzene

data are collected in Table 2. Figure 1b includes the ionization efficiency plot of *m*-chloro diazoaminobenzene obtained using thermolysis MIMS. Applying the methodology already described, the IE of *m*-chloro diazoaminobenzene and the *m*-chlorophenyldiazonium radical are found to be 9.46 ± 0.07 and 7.91 ± 0.07 eV, respectively. The probable accuracy of the measurements is indicated by the fact that the slopes of the ionization efficiency curves for *m*-chloro diazoaminobenzene radical cation, *m*-chlorophenyldiazonium cation, and the *m*-chlorophenyl cation are approximately equal to the slopes of the diazoaminobenzene radical cation, phenyldiazonium cation, and phenyl cation plots (Figure 1a), respectively, and that the curves also parallel each other. Comparing the IE and AE values for the phenyldiazonium radical and phenyl cation (7.89 eV, 8.50 eV) estimated in Figure 1a with those for the *m*-chloro substituted phenyldiazonium radical and phenyl cation (7.91 eV, 8.50 eV), we find the values to be identical, within experimental error. This confirms that the IE and AE values obtained for phenyldiazonium and phenyl radicals by thermolysis MIMS are internally

consistent, given that the *m*-chloro substituent is not expected to significantly alter the IE or AE of a compound. The behavior of the *p*-methoxy compound, where substituent effects are expected, is dramatic: there is a 2 eV difference in the IE of the radical and the diazoamino compound, demonstrating that the radical is indeed being sampled.

Because thermolysis is effective in producing the aryldiazonium radicals, it should also be producing anilino radicals [27–29] but we did not observe anilino radicals in the mass spectrum of the diazoaminobenzene pyrolysate. The reasons are not known: under the conditions of operation this radical may be thermally unstable or chemically reactive. However, anilino radicals were observed when sampling the pyrolysate from the *p*-methoxy substituted aminodiazonium compound. Figure 2 summarizes the ionization threshold data taken when sampling the pyrolysates of this compound. A notable feature of these ionization efficiency curves is the significant reduction (1.15 eV) in the IE of *p*-methoxy phenyldiazonium radical (6.74 eV) compared to that of the unsubstituted phenyldiazonium

Table 2. Measured ionization and appearance energies[a]

Type	Chemical species	IE or AE		Literature value
Diazoamino	p-CH$_3$OC$_6$H$_4$N$_3$HC$_6$HC$_4$OCH$_3$(p)	8.73		
Diazoamino	p-CH$_3$C$_6$H$_4$N$_3$HC$_6$H$_4$CH$_3$(p)	9.17		
Diazoamino	C$_6$H$_5$N$_3$HC$_6$H$_5$	9.27		
Diazoamino	m-ClC$_6$H$_4$N$_3$HC$_6$H$_4$Cl(m)	9.46		
Diazoamino	p-FC$_6$H$_4$N$_3$HC$_6$H$_4$F(p)	9.32		
Diazoamino	p-CH$_3$OC$_6$H$_4$N$_2$	6.74		(7.28)[c]
Diazoamino	p-CH$_3$C$_6$H$_4$N$_2$	7.72		
Diazoamino	C$_6$H$_5$N$_2$	7.89		
Diazoamino	m-ClC$_6$H$_4$N$_2$	7.91		
Diazoamino	p-FC$_6$H$_4$N$_2$	8.03		
Diazoamino	m-NO$_2$C$_6$H$_4$N$_2$	8.90		
Anilino	p-CH$_3$OC$_6$H$_4$NH	7.63		
Aryl	p-CH$_3$OC$_6$H$_4$	7.33	(+0.59)[b]	(8.32)[c]
Aryl	p-CH$_3$C$_6$H$_4$	8.31	(+0.59)[b]	
Aryl	C$_6$H$_5$	8.44	(+0.53)[b]	(8.1)[d]
Aryl	m-ClC$_6$H$_4$	8.50	(+0.59)[b]	
Aryl	p-FC$_6$H$_4$	8.54	(+0.51)[b]	

[a]By log-linear plot method vs. biphenyl, IE = 8.16 ± 0.13 eV.
[b]Difference between diazonium and aryl ion threshold energies.
[c]Reference 41.
[d]Reference 42.

radical (7.89 eV). This is expected, the p-methoxy group (weakly electron attracting by the inductive mechanism, strongly electron donating by resonance) stabilizes the charge. Figure 2 also shows that the sought after anilino radicals are generated. This follows from the fact that the measured ionization energy of p-OCH$_3$–C$_6$H$_4$NH$^+$, 7.63 eV, is well below that of the

parent neutral compound (8.73 eV). As expected, the anilino radical has a significantly higher ionization energy than the diazo radical generated concurrently. The detection of both of the complementary radicals in this case provides additional evidence that the radical products of thermolysis of the diazoaminoaromatic compounds are being sampled in these experiments.
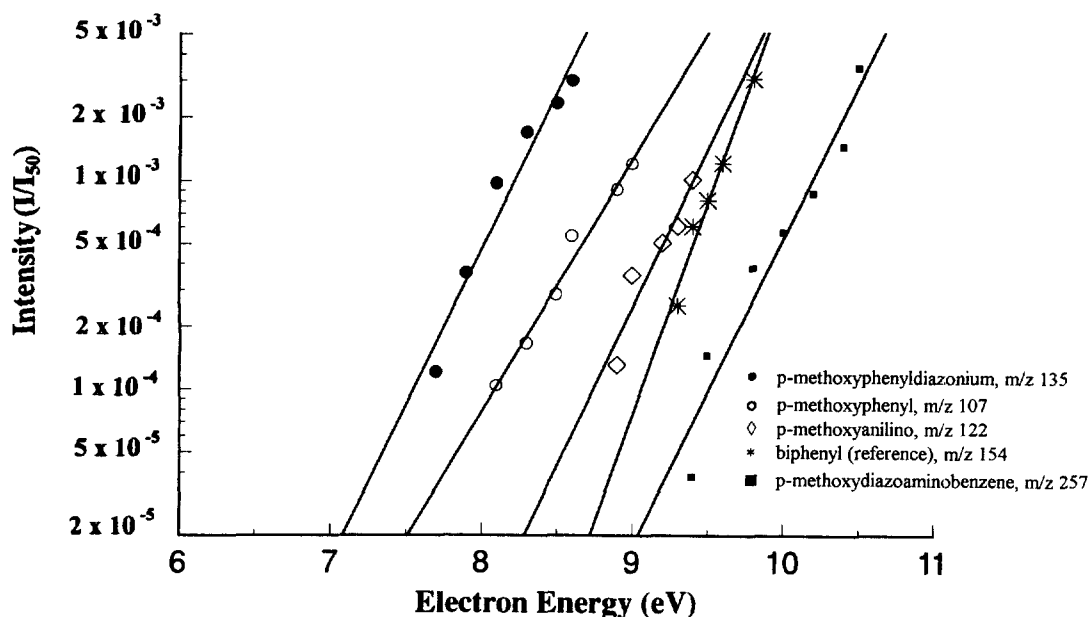

Figure 2. The ratio (I/I_{50}) of signal intensity (I) near threshold electron energy to that (I_{50}) at 50 eV plotted against electron energy for p-methoxyphenyldiazonium cation (filled circle, m/z 135, IE = 6.74 eV), p-methoxy phenyl cation (open circle, m/z 107, AE = 7.33 eV), p-methoxyanilino cation (diamond, m/z 122, IE = 7.42 eV), biphenyl radical cation (asterisk, m/z 154, IE = 8.16 eV) and bis(p-dimethoxyphenyl)diazoamino radical cation (filled square, m/z 257, IE = 8.73 eV) on a log-linear scale. The biphenyl radical cation (IE = 8.16 eV) was used as calibrant.

Sampling and studying phenyl radicals is a challenging task. It is possible that the pyrolysis/MIMS methodology might allow the detection of phenyl radicals produced either by fragmentation of the phenyldiazonium radicals before ionization (Scheme Ib) or by direct dissociation of the parent compound. The threshold energy values in Table 2 can be considered in determining whether or not phenyl (and substituted phenyl) radicals are being sampled or, alternatively, whether the observed phenyl cations are simply the products of ionic fragmentation. The experimental appearance energy for the phenyl cation itself is 8.44 ± 0.07 eV, a value which is consistent with its production by ionization of a phenyl radical, a process with a known ionization energy of 8.1 ± 0.1 eV [42]. On the other hand, according to Glaser and Horan [37], the energy required for dissociation of the phenyldiazonium cation to form a singlet phenyl cation and the neutral nitrogen molecule is about 1.1 eV. This gives an expected AE value of at least 8.99 eV when combined with the experimental value (7.89 eV) for the IE of the phenyldiazonium radical. This value is 0.5 eV greater than the measured threshold and it suggests that phenyl radicals, too, are being sampled by MIMS. The evidence for this is strengthened when the data for the substituted compounds is considered. All show threshold energies for the aryl ions which higher than the threshold energies for the diazonium ions by values that fall in the range 0.56 ± 0.03 eV. Either of two conclusions is possible: (i) this value (0.56 eV), rather than the literature value of 1.1 eV, represents the critical energy for dissociation of the phenyldiazonium ion by N_2 elimination or (ii) the aryl radicals are being generated and sampled by passage through the membrane prior to ionization. We favor the second explanation, in part due to the fact that the striking absence of a substituent effect on this energy difference is much more readily associated with the radical dissociation process (eq 3) than with the ionic dissociation process (eq 4):

(3)

(4)
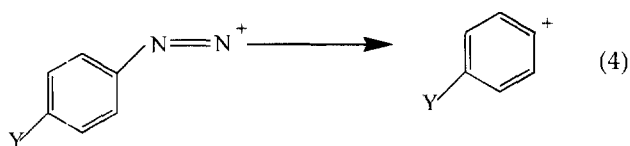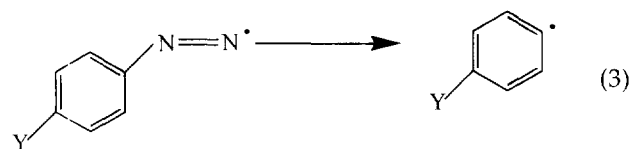
The correlation of IE of radicals with Hammett σ values [38] and Brown σ^+ values [39] has been previously studied by Harrison et al. [40]. Figure 3 plots the estimated IEs of the substituted phenyldiazonium radicals obtained using thermolysis MIMS against the
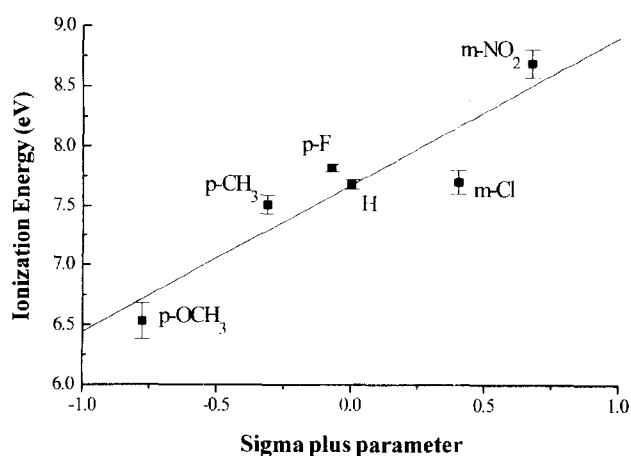

Figure 3. Ionization energies of substituted phenyldiazonium radicals plotted against Brown σ^+ values (from ref 40). The error bars represent the average deviation of triplicate measurements.

Brown σ^+ values. The linear correlation ($R^2 = 0.938$) demonstrates that the observed ion signals (at low electron energy) are indeed due to the radicals alone and validates the threshold energy measurements. It demonstrates that thermolysis-MIMS methodology is indeed useful for studying radical intermediates in a reaction medium. We note that the correlation of the p-methoxyphenyldiazonium radical is much better when Brown σ^+ values are used, compared to the plot against Hammett σ values.

Conclusion

By combining a pyrolysis apparatus with a membrane introduction system, it is possible to sample free radicals using mass spectrometry. In particular, the applicability of on-line MIMS sampling of aryldiazonium, anilino, and aryl radicals from a gaseous reaction medium is demonstrated. The detection of both of the complementary radicals arising from cleavage of the weak N–N bond in this case demonstrates that the radical products of thermolysis of the diazoaminoaromatic compounds are being sampled in these experiments. The identification of the diazo and anilino radicals is based on threshold energy measurements which demonstrate that the ionization of the radicals not the fragmentation of the molecular ions of the diazoamino parent compounds, is responsible for the observed ionic signals. In addition, the thermochemical data demonstrate that the aryl radicals are sampled from the pyrolysate. It must be remembered in each of these cases that the ions observed in the mass spectra recorded at higher electron energies will contain significant contributions from normal ionic fragmentation processes.

The measurement of thermochemical properties of these free radicals is an additional result of this study. It should be possible to extend the methodology described here to the study of other free radicals. In

favorable cases, an estimate of the approximate lower limit on the life time of the free radical might be possible with this methodology. The wide linear dynamic range, on-line monitoring capability, and the simplicity of MIMS makes it an attractive method for sampling and studying free radicals.

Acknowledgments

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